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AIR POLLUTION ASPECTS OF HYDROGEN SULFIDE

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Litton Systems, Incorporated
Bethesda, Maryland

September 1969

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AIR POLLUTION ASPECTS

OF

HYDROGEN SULFIDE

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Services
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Compiled by Sydney Miner

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September 1969

FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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ABSTRACT

Hydrogen sulfide gas is very toxic to humans and at concentrations over 1,000,000 μg/m³ quickly causes death by paralysis of the respiratory tract. At lower concentrations it causes conjunctivitis with reddening and lachrymal secretion, respiratory tract irritation, pulmonary edema, damage to heart muscle, psychic changes, disturbed equilibrium, nerve paralysis, spasms, unconsciousness, and circulatory collapse. One outstanding episode in Mexico involving accidental release of hydrogen sulfide killed 22 people and 50 percent of the exposed animals and hospitalized 320 persons. The gas has a very obnoxious odor at low concentrations (1 to 45 μg/m³). At concentrations below 60,000 μg/m³ it has very little effect on plants. Hydrogen sulfide also tarnishes silver and copper and combines with heavy metals in paints to discolor or darken the paint surface.

The primary natural source of hydrogen sulfide is biological decay of protein material in stagnant water. Industrially, hydrogen sulfide is a by-product of many processes. Main industrial producers are kraft paper mills, oil refineries, natural gas plants, and chemical plants manufacturing sulfur-containing compounds. Hydrogen sulfide is also produced in sewers and sewage disposal plants. Average concentrations of hydrogen sulfide in urban atmospheres are reported to range from 1 to 92 μg/m³, with most urban averages reported at less than 10 μg/m³.

The installation of black liquor oxidation systems and scrubbers has substantially reduced emissions from kraft paper mills. Wet scrubbers using various absorbents and iron oxide are used in refineries, natural gas plants, coke ovens, and chemical plants to remove hydrogen sulfide from gas streams. Incineration is also used to reduce emissions of the gas.

Hydrogen sulfide corrosion of silver has required substitution of gold contacts in electrical appliances at an estimated increased cost of $14.8 million during 1963. Abatement of air pollution resulting from the pulp and paper industry, in which hydrogen sulfide is a major factor, has cost approximately $10 million per year and is predicted to increase to $15 million per year in the immediate future. Major expenditures have been made by refineries and natural gas plants to remove hydrogen sulfide from sour gases and to recover sulfur as a valuable by-product.

Analytical techniques based on the methylene blue and molybdenum blue methods are available for laboratory analysis of hydrogen sulfide. The spot method for measuring hydrogen sulfide, based on tiles or paper impregnated with lead acetate, is also widely used.

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1. INTRODUCTION

Hydrogen sulfide (H_2S) is a colorless gas that has an obnoxious odor at low concentrations. The odor threshold is in the µg/m^3 range. In higher concentrations, the gas is toxic to humans and animals and corrosive to many metals. It will tarnish silver and react with heavy metals in paints to discolor the paint. In humans, it will cause headache, conjunctivitis, sleeplessness, pain in the eyes, and similar symptoms at low air concentrations and death at high air concentrations. However, the majority of the complaints arising from hydrogen sulfide air pollution are due to its obnoxious odor in extremely low air concentrations.

Air pollution by hydrogen sulfide is not a widespread urban problem but is generally localized in the vicinity of an emitter such as kraft paper mills, industrial waste disposal ponds, sewage plants, refineries, and coke oven plants.

2. EFFECTS

2.1 Effects on Humans

Hydrogen sulfide, which is very toxic to humans, generally enters the human body through the respiratory tract, from which it is carried by the blood stream to various body organs. The hydrogen sulfide that enters the blood can lead to blocking of oxygen transfer, especially at high concentrations.[102] In general, the hydrogen sulfide acts as a cell and enzyme poison and can cause irreversible changes in nerve tissue.[34,101]

At high concentrations (over 1,000,000 $\mu g/m^3$), hydrogen sulfide frequently causes death quickly by paralysis of the respiratory center.[101] However, if the victim is moved quickly to uncontaminated air and respiration initiated before heart action stops, rapid recovery can be expected.[99] At lower concentration, hydrogen sulfide causes conjunctivitis, lachrymal secretion, respiratory tract irritation, pulmonary edema, damage to the heart muscle, psychic changes, disturbed equilibrium, nerve paralysis, spasms, unconsciousness, and circulatory collapse.[101,102] Some common symptoms are metallic taste, fatigue, diarrhea, blurred vision, intense aching of the eyes, insomnia, and vertigo.[49,101] Some of the effects of hydrogen sulfide and the air concentrations at which they occur are shown in Table 15 in the Appendix.

Hydrogen sulfide may produce synergistic effects in mixtures with carbon disulfide hydrocarbons and carbon monoxide.[101] In Russia, an increased effect was attained with a mixture of hydrogen sulfide and naphtha gas.[102] In addition, mixtures of carbon monoxide and hydrogen sulfide in concentrations* that individually would not be dangerous were harmful to animals after only 10 minutes' exposure.[102]

2.1.1 Odor Threshold

Hydrogen sulfide has a characteristic smell of rotten eggs,[114] and this odor is the most sensitive indicator of its presence in low concentrations. However, the odor perception threshold varies considerably among individuals and apparently depends on the age and sex of the individuals, the size of the town they live in, and whether they smoke.[3] The reported odor threshold varies between 1 and 45 μg/m³ (see Table 1). At 500 μg/m³, the odor is distinct; at 4,000 to 8,000 μg/m³, the odor is offensive and moderately intense; and at 30,000 to 50,000 μg/m³, the odor is strong but not intolerable.[99] At 320,000 μg/m³, the smell is not as pungent, probably due to the paralysis of the olfactory nerves.[102] The perception concentrations are based on initial inhalations since continuous inhalation causes rapid olfactory sense fatigue.[99] At concentrations over 1,120,000 μg/m³, there is practically no sensation of odor and death can occur rapidly.[101] Loss of sense of smell has even been reported at 150,000 μg/m³ after exposures of from 2 to 15 minutes.[132] Therefore, dulling of the olfactory nerves constitutes a major danger to people who are exposed to moderate and high concentrations of hydrogen sulfide for extended periods.[102]

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*Values not stated.

2.1.2 Pollution Occurrences

The most serious episode reported involving hydrogen sulfide air pollution occurred in Poza Rica in Mexico on November 24, 1950. There was an accidental release of gas from a hydrogen sulfide absorption unit in a natural gas refining plant.[65] This resulted in the release of considerable amounts of hydrogen sulfide, which quickly spread to the residential areas where most people were asleep. The situation was aggravated by an atmospheric temperature inversion with patches of haze and fog. The gas was shut off within 20 to 25 minutes, yet 22 persons died and 320 persons were hospitalized as a result of this brief exposure.[5,50] The effects were characteristic of hydrogen sulfide gas poisoning: loss of sense of smell, cough, dyspnea, conjunctival irritation, nausea, vomiting, severe headache, and vertigo.[50] The incident was over before any atmospheric measurements were made.

In the Terre Haute, Ind., episodes in May and June

TABLE 1

ODOR DETECTION THRESHOLD FOR HYDROGEN SULFIDE

Odor Threshold ($\mu g/m^3$)	Reference
9-45	3
7.1[a]	78
.71[b]	78
15	75
6.8[c]	142
12-30	41

---

[a] Hydrogen sulfide from sodium sulfide.

[b] Hydrogen sulfide gas.

[c] Mean value ratio of highest to lowest odor threshold concentration detected by all observers in successive tests is 3.18.

1964, hydrogen sulfide concentrations were sufficient to cause foul odor, resulting in 81 public complaints of discomfort and paint-blackening. Of the complaints, 40 referred to property damage, and 41 referred to health effects. The main symptoms reported were nausea, loss of sleep and abrupt awakening, shortness of breath, and headaches. However, almost none of those affected sought medical attention. The source of the hydrogen sulfide was a 36-acre lagoon used for biodegradation of industrial wastes. Hydrogen sulfide concentrations in the atmosphere during the episodes ranged between 34 and 450 $\mu g/m^3$.[7]

A major pollution problem of kraft mills is the emission of hydrogen sulfide and organic sulfide, causing a disagreeable odor in the surrounding areas. At times atmospheric concentration of these gases adjacent to the kraft mills have reached levels which are capable of producing nausea, vomiting, headache, loss of appetite, disturbed sleep, upset stomach, and hampered breathing.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

Hydrogen sulfide produces about the same health effects in domestic animals as in man at approximately the same air concentrations.[101] The Air Pollution Control Association Committee on Ambient Air Standards[76] stated (1964) that spontaneous injury to animals occurs at 150,000 to 450,000 μg/m³ of hydrogen sulfide. In the Poza Rica incident, it was reported that all the canaries in the area were killed and about 50 percent of the other animals died. Among these were chicken, cattle, pigs, geese, dogs, and cats.[33,66]

2.2.2 Experimental Animals

Fyn-Djui[41] exposed 10 rats to 1,000 μg/m³ of hydrogen sulfide in chronic experimental conditions for 12 hours per day for three months. The exposure produced changes in the functional state of the central nervous system, irritations in the mucosa of the trachea, and morphologic changes in the brain cortex. At concentrations of 20 μg/m³, only slight to negligible changes occurred in the functional state of the nervous system, and there was barely perceptible irritation to the mucosa of trachea and bronchi.[41] Weedon et al.[139] exposed houseflies to hydrogen sulfide concentrations of 1,500,000 μg/m³. The percent of kill versus time of exposure is shown in Figure 1. They also exposed groups of eight rats and four mice to hydrogen sulfide concentrations of 1,500,000 μg/m³, 380,000 μg/m³, 96,000 μg/m³, and 24,000 μg/m³ for periods up to 16 hours. At 1,500,000 μg/m³ all the rats were active during the first 5 minutes. At the end of 5 minutes they lost their muscular coordination, and by 11 minutes they were prostrate. They all died in 29 to 37 minutes. Similarly, the mice were active during

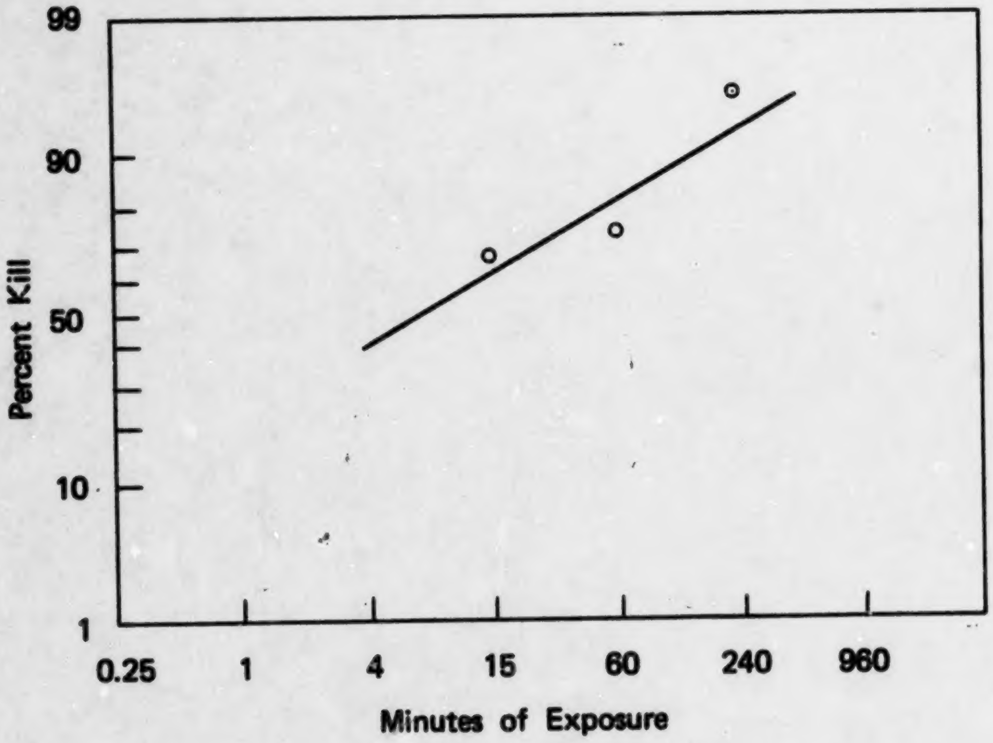


FIGURE 1

Time-Mortality Toxicity Curve for Houseflies Exposed to 1,500,000 µg/m³ Hydrogen Sulfide[139] the first few minutes. Marked lachrymation followed and all died within 20 minutes.

At exposures of 380,000 μg/m³ all the rats were active, sniffing and rubbing their noses for the first 25 minutes, and then they became quiet. Three rats were dead when the experiment was discontinued at 22.9 hours. The mice exposed to the same concentrations exhibited the same symptoms for the first hour of exposure. At the end of 2 hours they were gasping and their abdomens were distended. They all died at the end of 7 hours.

The rats were not affected during the first hour of exposure to 96,000 μg/m³. Even after 16 hours, the surviving rats seemed to be in fair condition, even though they were lethargic and gasping. The mice exposed to the same concentrations showed similar but more marked signs. Only one mouse survived after 16 hours' exposure, and it died 23 hours later.

No abnormal symptoms were noticed at 24,000 μg/m³. A mouse exposed to the 24,000 μg/m³ concentration for 16 hours was sacrificed, and at autopsy all organs proved normal throughout. The time required to reach a 50 percent mortality (TL_{50}) rate in these experiments for the rats, mice, and flies is shown in Table 16 in the Appendix. Typical gross findings at autopsy for exposed rats and mice are shown in Table 17 in the Appendix.

Patty[99] reported an experiment in which a dog was exposed to 1,500,000 μg/m³ of hydrogen sulfide. When first placed in the atmosphere, the dog was frisky for a short time; he then stopped, breathed laboriously for a moment, fell, gasped, and remained motionless with legs extended. At the end of 1 minute he was removed and given artificial respiration, and he recovered fully in 1 to 2 minutes.

Smith and Gosslen[120] found that pretreatment of mice with sodium nitrate and p-aminopropinphenone (PAPP) significantly prolonged their survival during continuous exposure to hydrogen sulfide. The mice were exposed to 1,100,000 μg/m³, 1,500,000 μg/m³, and 2,840,000 μg/m³; the greatest protection occurred at the intermediate concentration as shown in Table 2. Propylene glycol also prolonged the life of the mice. For the propylene glycol to be effective at the middle concentration (1,100,000 μg/m³), exposure to hydrogen sulfide has to be delayed for 30 minutes after treatment. At the highest concentration (2,840,000 μg/m³), propylene glycol did not have any effect, even when exposure to the hydrogen sulfide was delayed 30 minutes.

Baikov[17] found that there were no noticeable adverse effects to rats after exposure for 70 days, 24 hours per day, to air containing 8 μg/m³ of hydrogen sulfide and 10 μg/m³ carbon disulfide (the Russian environmental standard).

TABLE 2

THE PROTECTION INDEX* OF SODIUM NITRITE AND PAPP PRETREATED MICE EXPOSED TO HYDROGEN SULFIDE[120]

(Total Number of Mice = 107)

Pretreatment	Hydrogen Sulfide (ppm) 722	985	1,872
Nitrite	2.3	3.8	1.4
PAPP (no delay)	1.6	3.5	2.4
PAPP (30-minute delay)		1.3	2.2

$$\text{*Protection index} = \frac{\text{mean survival time of protected mice}}{\text{mean survival time of control mice}}$$

2.3 Effects on Plants

There is little evidence that hydrogen sulfide causes significant injury to field crops at environmental air concentrations.[66,123]

McCallan[84] observed that little or no injury occurred to 29 species of plants when they were fumigated with less than 60,000 μg/m³ of hydrogen sulfide for 5 hours. After 5 hours at 600,000 μg/m³, some species were injured, but not all. Boston fern, apple, cherry, peach and coleus showed no appreciable injury at concentrations below 600,000 μg/m³. At concentrations between 60,000 and 600,000 μg/m³, gladiolus, rose, castor bean, sunflower, and buckwheat showed moderate injury. Slightly more sensitive were tobacco, cucumber, salvia, and tomato.[84,148]

In general, hydrogen sulfide injures the youngest plant leaves rather than the middle-aged or older ones. Young, rapidly elongating tissues are the most severely injured. Typical exterior symptoms are wilting without typical discoloration (which starts at the tip of the leaf), with the scorching of the youngest leaves of the plant occurring first.[134,135]

Thornton and Setterstrom[136] exposed tomato plants, buckwheat, and tobacco to air concentrations of ammonia, chlorine, sulfur dioxide, hydrogen cyanide, and hydrogen sulfide of 1,500, 6,000, 24,000, 96,000, 380,000, and

1,500,000 μg/m³ for periods of 1, 4, 15, 60, 240, and 960 minutes. They found that hydrogen sulfide was only mildly toxic to plant tissue. They also made measurements of pH changes in leaf and stem tissue of tomato plants. At low hydrogen sulfide concentrations, they found no significant changes in pH. At high hydrogen sulfide concentrations (1,500,000 μg/m³) the whole plant showed only a slight drop in pH. Once the pH changed, there was no recovery. They found very little correlation between the hydrogen sulfide-caused pH change and plant damage.

The time in minutes until 50 percent of the exposed plant surfaces were injured at 1,500,000 μg/m³ of hydrogen sulfide is shown in Table 3.

Barton[19] exposed dry and soaked radish and rye seeds to hydrogen sulfide in concentrations of 380,000 μg/m³ and 1,500,000 μg/m³ for periods of 1, 4, 15, 60, 240, and 960 minutes. He found that the gas is relatively nontoxic to the seeds. The germination percentages for both rye and radish were similar to the control lots, and there was no delay in germination for the dry seeds. Germination for the soaked seeds of both rye and radish was delayed 4 to 6 hours after 240 minutes' exposure and 21 to 24 hours after 960 minutes' exposure to 1,500,000 μg/m³. At 380,000 μg/m³, soaked radish seed had no delay in germination, but a 28-hour delay in germination of soaked rye seed resulted from a 960-hour exposure at 1,500,000 μg/m³.

TABLE 3

TIME IN MINUTES UNTIL 50 PERCENT INJURY TO EXPOSED PLANT SURFACES AT 1,500,000 μg/m^3 HYDROGEN SULFIDE[136]

Plant Surface	Plant	Time in Minutes
Leaves	Tomato	30
	Buckwheat	60
	Tobacco	100
Stems	Tomato	45
	Buckwheat	120
	Tobacco	480

Benedict and Breen[20] fumigated 10 weeds which occur widely throughout the United States with hydrogen sulfide and other pollutant gases in an effort to develop a method for identifying the pollutants causing damage in an area. These plants included annual bluegrass, cheeseweed, chickweed, dandelion, Kentucky bluegrass, lamb's-quarters, mustard, nettle-leaf goosefoot, pigweed, and sunflower, which they fumigated with 150,000 $\mu g/m^3$ and 750,000 $\mu g/m^3$ of hydrogen sulfide for about 4 hours. The hydrogen sulfide always produced the greatest amount of marking on the youngest leaves. Very often the growing point was killed. The marking occurred between the veining network on the broad-leaved plants.

The narrow-leaved plants developed a general powdery appearance between the tip and the bend of the leaf, except in extreme cases where the entire leaf was killed.

The color of the marking was usually white to tan, except for sunflowers, where the leaves in the bud stage took on an orange-brown cast. The percentage of the leaf marked by hydrogen sulfide is shown in Table 18 in the Appendix.

The six-week-old plants in dry soil showed more marking at the higher hydrogen sulfide concentration than the plants in wet soil, while the reverse effect occurred at the lower concentration, indicating that drought conditions may increase the plant's sensitivity to concentrations of 750,000 μg/m³ hydrogen sulfide and decrease it to concentrations of 150,000 μg/m³. The relative sensitivity of the 10 species to hydrogen sulfide is shown in Table 19 in the Appendix.

2.4 Effects on Materials

2.4.1 Effects on Paint

Hydrogen sulfide in the atmosphere reacts with paints containing heavy metal salts in the pigment and the drier to form a precipitate which darkens or discolors the surface. Lead, mercury, cobalt, iron, and tin salts cause a gray or black discoloration; cadmium salts cause a yellowish-orange discoloration. Lead is probably the most common metal to exhibit discoloration caused by the formation of black lead sulfides.[54,145] The most commonly used white pigment in the past was basic lead carbonate. Recently, titanium dioxide pigments have been replacing the use of lead carbonate by the paint industry. However, lead pigments continue to be used because of the added durability they impart to paint films.

Wohlers and Feldstein[145] reported that experiments in the Bay Area of California showed that old lead-base paints are more susceptible to hydrogen sulfide damage than are new ones. They also reported that darkening is dependent on both duration of exposure and concentration and can occur after exposure to hydrogen sulfide concentrations as low as 75 $\mu g/m^3$ for two hours. The time-concentration relationship for paint-blackening is shown in Figure 2. These authors suggested that paint darkening by hydrogen sulfide may vary depending on (1) heavy metal content in paint, (2) temperature and moisture, (3) hydrogen sulfide concentration, (4) age and condition of paint, and (5) presence of other contaminants in the air.

Manganelli and Gregory[81] found that the extent of darkening of basic lead carbonate films by hydrogen sulfide increased as the relative humidity increased from 30 to 90 percent. They also showed that the darkening for lead carbonate films on wood was less than on tile.[81]

White lead paints darkened by hydrogen sulfide often revert to their original color by oxidation of the sulfide to white sulfate.[147] Manganelli and Gregory[81] found that darkened films of basic carbonate faded in the presence of light and oxygen and that the fastest rates of fading were obtained in sunlight or under a tungsten lamp. They also found that the fading capacity of fresh paint was not dependent on the presence of atmospheric oxygen, indicating that an oxidizing substance such as a peroxide was formed during the drying of the film.

Paint-darkening by hydrogen sulfide occurred in the Jacksonville area of Florida in 1961 due to hydrogen sulfide

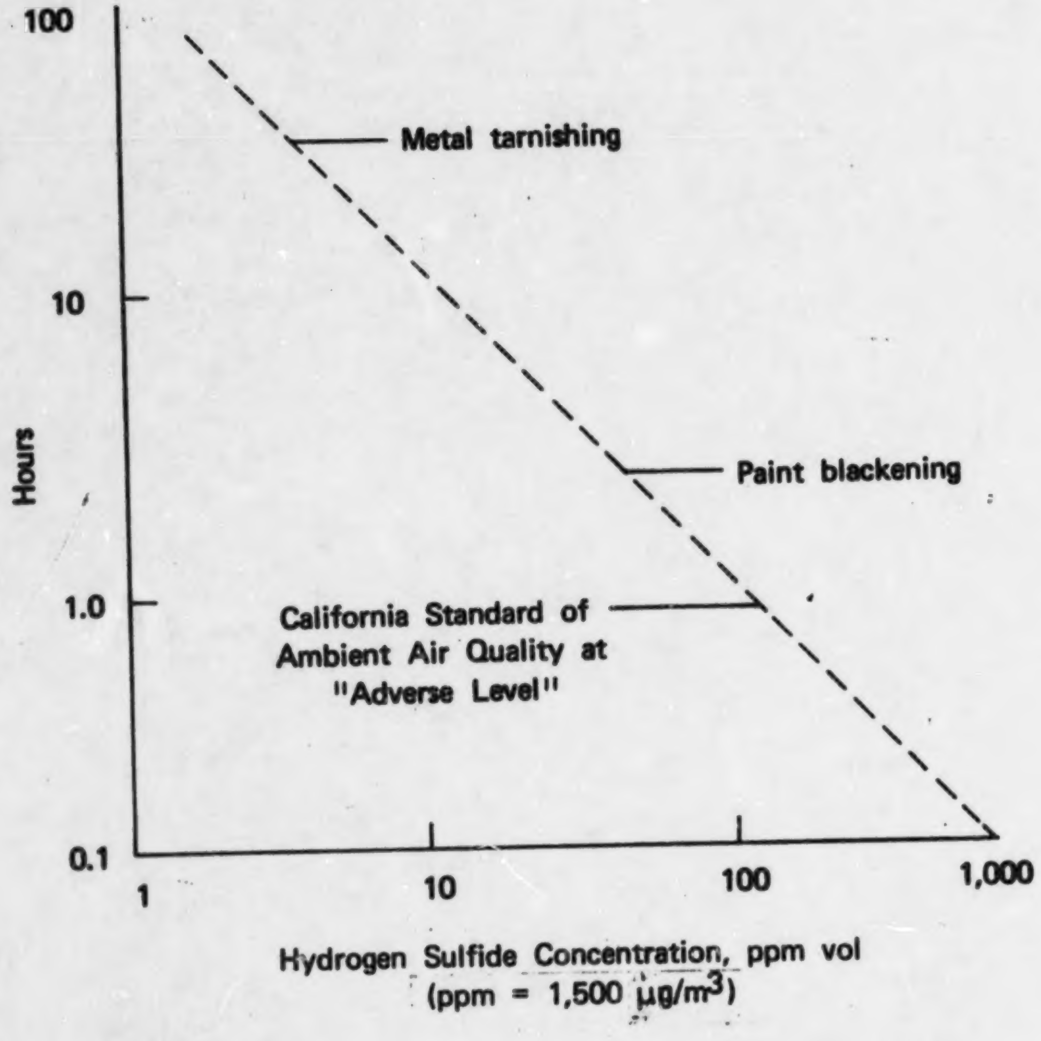


FIGURE 2

Exposure Time Versus Concentration for Hydrogen Sulfide Effects[145] emitted from the city water aeration plant.[117] Paint-darkening also occurred in 1963 in New York City and in South Brunswick, N.J. In the New York incident, the hydrogen sulfide was released from a polluted salt water channel. An industrial dump was responsible for the incident in New Jersey. In Terre Haute, Ind., paint on houses close to the industrial waste disposal lagoon was darkened,[7] and in the communities of Lewiston, Idaho, and Clarkston, Wash., damage to house paint was caused by hydrogen sulfide emissions from a kraft paper mill.[127]

2.4.2 Effects on Metals

In the presence of hydrogen sulfide, copper and silver tarnish rapidly.[147] Copper that has been exposed to unpolluted air for some time resists attack by hydrogen sulfide.[123] Hydrogen sulfide tarnishes silver at room temperature; however, both moisture and oxygen must be present for tarnishing to occur.[46,123] The sulfide coating formed on copper and silver electrical contacts can increase contact resistance when the contacts are closed. In some cases, this can result in the contacts becoming welded shut.[147] Wohlers and Feldstein[145] indicated that hydrogen sulfide-sensitive metals, like silver or copper, will tarnish when exposed to hydrogen sulfide concentrations above 4 $\mu g/m^3$ for 40 hours (Figure 2).

Some alloys of gold--even such a high-carat alloy as 69 percent gold, 25 percent silver, and 6 percent platinum--will tarnish when exposed to hydrogen sulfide. However, in general, gold (14-carat and above) and gold leaf (95 percent gold and above) will have adequate resistance to atmospheric hydrogen sulfide.[67]

Hydrogen sulfide will attack zinc at room temperature, forming a zinc sulfide film which prevents further corrosion. At high temperatures the attack is quite vigorous.[70] At concentrations normally found in the atmosphere and at ambient temperatures, hydrogen sulfide is not corrosive to ferrous metals.[118]

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists (ACGIH), at their 29th Annual Meeting in 1967, set the threshold limit value for hydrogen sulfide in air for an eight-hour-day, 40-hour week, at 15,000 $\mu g/m^3$.[137] The hydrogen sulfide ambient air quality standards for various States and governments are shown in Table 4.

TABLE 4

AMBIENT AIR QUALITY STANDARDS

Country or State	Basic Standard		Permissible Standard		Maximum single Measurement $\mu g/m^3$	Reference
	$\mu g/m^3$	Avg Time	$\mu g/m^3$	Avg Time		
California	150	1 hr				67, 125, 132
Missouri	45	30 min	75	30 min		9, 67, 125
Montana	45	30 min	75	30 min		125
New York	150	1 hr				125
Pennsylvania	7.5	24 hr	150	1 hr		12, 22, 125
Texas	120	30 min	180	30 min		125
Czechoslovakia	8	24 hr	8	30 min	8	67, 125
Canada (Ontario)	45	30 min				125
Poland	20	24 hr				62, 100, 125
U.S.S.R.	8	24 hr	8	20 min	8	93, 125
Federal Republic of Germany	150	30 min	300	30 min		103, 125

3. SOURCES

3.1 Natural Occurrence

Hydrogen sulfide is produced in nature primarily through decomposition of proteinaceous material (vegetable and animal) by bacteria.[81,101] It develops principally in stagnant and insufficiently aerated water such as found in swamps and polluted water.[34,35,101] Hydrogen sulfide also occurs naturally as a constituent of natural gas, petroleum, sulfur deposits, and numerous volcanic gases and sulfur springs.[70,81,101]

Robinson and Robbins[108] have estimated that the annual worldwide production of hydrogen sulfide is around 90 to 100 million tons, with 60 to 80 million tons coming from land sources and 30 million tons coming from ocean areas. Other estimates range as high as 202 million tons from ocean areas and 82 million tons from land areas.[108] Data on background air concentrations of hydrogen sulfide due to the natural sources are scarce. However, it has been estimated to be between 0.15 and 0.46 $\mu g/m^3$, which is well below the odor threshold or the concentrations at which deleterious effects are known to occur.

3.2 Production Sources

Hydrogen sulfide is produced as a by-product in many industrial processes. Production sources include the petroleum industry (refineries and natural gas plants), petrochemical plant complexes, coke oven plants, kraft paper mills, chemical processing industries, dye manufacture, viscose rayon manufacture, sulfur production, manufacture of sulfur-containing chemicals, iron and metal smelters, food processing plants, and tanneries.

3.2.1 Petroleum Industry

Sulfur enters the refinery as a constituent of crude oil and is usually found in combination with hydrogen as hydrogen sulfide and with hydrocarbons as various organic sulfides. Since removal of sulfur from both product and intermediate stocks is necessary to meet low sulfur requirements for fuel oil and to prevent sulfur poisoning of catalysts, processes such as hydrogen treating are employed. During the various steps employed in processing the crude oil, the sulfur compounds are generally converted to hydrogen sulfide and lower molecular weight mercaptans.[15,57] From each 20,000 barrels of crude oil with high sulfur content processed, approximately 50 tons of hydrogen sulfide are formed.[81]

The main sources of air pollution in refineries are untreated gas stream leaks, vapors from crude oil and raw distillates, and process and condensate sewers.[104] Typical refinery processing systems that have hydrogen sulfide emissions are cracking units, catalytic reforming units,[88] and sulfur recovery units.[138] The cracking process tends to convert sulfur contained in crude oil into hydrogen sulfide in the heavier materials and into mercaptans in the gasoline fractions.[140] Measurements were made in the El Paso, Tex., area of the atmospheric hydrogen sulfide concentration adjacent to an oil refinery. The mean hydrogen sulfide concentration was 6 μg/m³. This varied from undetectable amounts to a maximum of 91 μg/m³.[55]

In 1960 there were about 300 oil refineries distributed throughout the United States with a crude oil capacity of approximately 10 million barrels per day.[132] By 1969 there were approximately 263 refineries in the United States with a crude oil capacity of approximately 12 million barrels per day.[130] The States in which the refineries are located and their crude charge capacity in January 1969 are shown in Table 20 in the Appendix. The crude capacity of refineries in the United States from 1964 projected to 1972 is shown in Figure 3.

A number of refineries and natural gas plants have installed units to recover sulfur from hydrogen sulfide. The plant capacities and yearly production rate for this process are shown in Table 5.

TABLE 5

SULFUR PRODUCTION FROM HYDROGEN SULFIDE
IN THE UNITED STATES[48,94]

	Long Tons/Year	
Year	Plant Capacity	Actual Production
1961	1,659,000	858,000
1967	2,737,000	1,244,000
1968	3,036,000	1,400,000

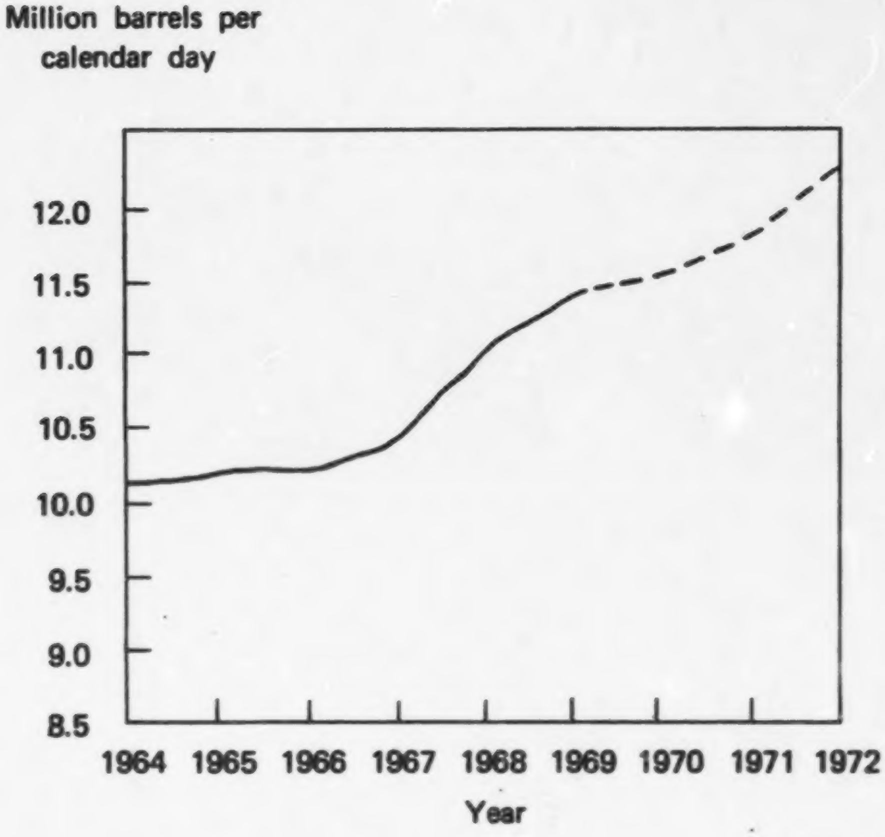


FIGURE 3

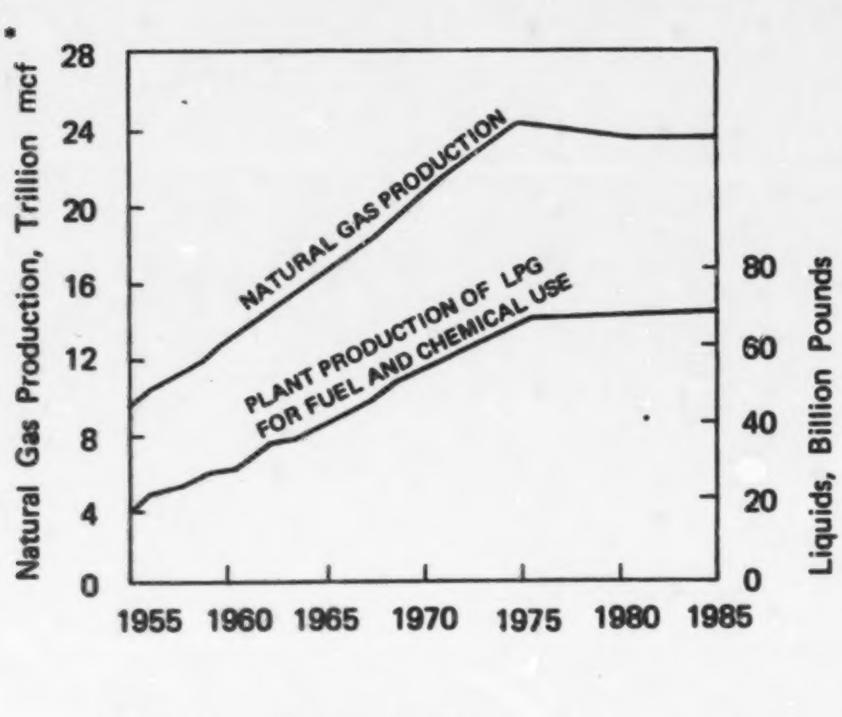
Crude Capacity of United States Refineries[95]

Hydrogen sulfide occurs naturally in many areas in association with natural gas.[101] In some areas, such as Alberta, Canada, the sour natural gas can consist of over 50 percent hydrogen sulfide. In processing, the natural gas stream is treated to remove the hydrogen sulfide, which is generally converted to sulfur. Distributing companies which sell the natural gas for heating and power generation generally require that its hydrogen sulfide content be less than 23,000 µg/m³.[115] The amount of natural gas produced in the United States in 1955 (projected through 1985) is shown in Figure 4.

Another possible source of hydrogen sulfide air pollution in the petroleum industry is the production of asphalt. Mel'ster _et al_.[87] have reported that during the distillation and oxidation of petroleum for the production of asphalt, hydrogen sulfide is produced, but they gave no production or emission data.

3.2.2 Petrochemical Plant Complexes

Hydrogen sulfide is produced in petrochemical plants during cracking and other desulfurization reactions.[88] Krasovitskaya _et al_.[71] reported on atmospheric hydrogen sulfide concentrations around a petrochemical industrial complex in Russia. The complex consisted of three oil refineries, a synthetic alcohol plant, a chemical plant, and three power plants. Measurements made of air concentrations



* mcf : million cubic feet

FIGURE 4

Natural Gas Production and Plant Production of Ethane and Liquid Propane Gas (LPG) for Fuel and Chemical Use[56] of hydrogen sulfide showed 17 to 150 $\mu g/m^3$ inside the industrial complex, 8 to 70 $\mu g/m^3$ at 2.5 km from the complex, and 1 to 50 µg at 20 km from the complex.[71]

3.2.3 Kraft Mills

Hydrogen sulfide and organic sulfide are produced and released to the atmosphere in kraft mills in a number of locations. This emission imparts the characteristic odor in the vicinity of kraft paper mills and has been the cause of major air pollution problems. Over 50 percent of the pulp produced in the United States comes from the kraft or sulfate process.[68] Robinson and Robbins[108] estimated that in 1960 about 64,000 tons of hydrogen sulfide were emitted from kraft paper mills throughout the world.

In the kraft process, wood chips and a solution of sodium sulfide and sodium hydroxide (white liquor) are cooked in a digester for about 3 hours at elevated temperatures and pressures. The solution dissolves the liquor from the wood. The spent liquor (black liquor) is then separated from the cellulose fiber in the blow tank. The fiber is then washed and processed into paper. The remainder of the process involves the recovery and regeneration of the cooking chemicals from the black liquor. The recovery process is initiated by concentrating the black liquor by evaporation. The concentrated black liquor is then burned in the recovery furnace, and the inorganic chemicals collect on the floor of the furnace in a molten state (smelt). Hot combustion gases from the recovery furnace are used in the direct contact evaporation to concentrate the black liquor.[68,125]

The major sources of hydrogen sulfide emission in kraft mills are the stack gases from the recovery furnace, including the direct contact evaporator; the stack gases from the lime kilns;[29] and the noncondensibles from the digester relief, the blow tank, and the multi-effect evaporator.[21,127] The quantities of emissions from each source are given in Table 6. The amount of these emissions actually reaching the environment depends upon the efficiency of each of the abatement systems that are installed and operating at each mill. Table 7 shows the emissions from a kraft mill in Lewiston, Idaho. The mill produces 450 tons per day of bleached paper board and 200 tons per day of market pulp.[127]

The single largest source of hydrogen sulfide in a kraft mill is the recovery furnace, and the amount produced is very sensitive to furnace loading. The hydrogen sulfide produced in the furnace rises very rapidly when the furnace is operated above design conditions. The relationship between hydrogen sulfide production in the recovery furnace and the furnace loading is shown in Figure 5.

Measurements were made during a six-month period in 1961 and 1962 of ambient hydrogen sulfide concentration in the Lewiston, Idaho area, where the paper mill is the major

TABLE 6

HYDROGEN SULFIDE EMISSIONS FROM KRAFT MILL PROCESSORS

Sources	Pounds/Dry Ton Produced	$\mu g/m^3$ Emitted	Ref.
Digester blow (cooking time 3.75 hr, temp 172°C, sulfidity 22%)	0-0.45	0-600,000	68
Digester relief and blow (no data on conditions)	0.43	208,000	141
Digester blow (no data on conditions)	0.9		106
Digester relief and blow (cooking time 3.45 hr, temp 172°C, sulfidity 22.5%)	0.66		127
Digester relief (no data on conditions)	0.01-0.05		116
Recovery furnace	3.6-28	198,000-1,500,000	68,116
Recovery-furnace stack gases		750,000-1,150,000	141
Recovery furnace	9.0		106
Multiple-effect evaporators (potential)	1.2		68
Multiple-effect evaporators (normal)	0-0.06		68
Multiple-effect evaporators	1.2		106
Lime kiln		0-900,000	125

TABLE 7

ESTIMATED HYDROGEN SULFIDE EMISSIONS* FROM 650 TON/DAY KRAFT MILL IN LEWISTON, IDAHO[127]

Process or Equipment Source	lb/day
Digester gases	9
Evaporators	390
Recovery furnaces	3,120
Lime kilns	737
Total	4,256

*Includes oxidation towers for black liquor and chlorination for digester gases (see Abatement, Section 4).

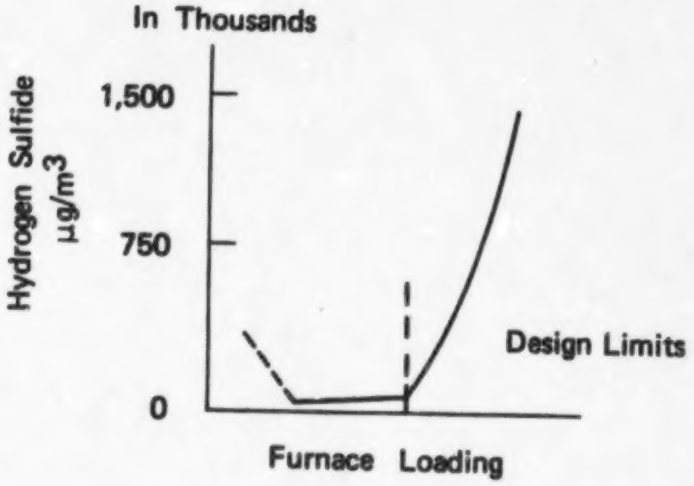


FIGURE 5

Relation Between Hydrogen Sulfide Production and Furnace Loading[125] contributor of gaseous pollutants. The measurements are summarized in Table 8. During an incident in November 1961, peak 2-hour concentrations of 77 μg/m³ were measured.[29]

TABLE 8

FREQUENCY DISTRIBUTION OF HYDROGEN SULFIDE CONCENTRATIONS, 1961-1962[29]

Hydrogen Sulfide Concentration (μg/m³)	%Frequency at Sampling Station		
	Lewiston Orchards	Lewiston Residential District	Lewiston Commercial District
0-3	92.2	89.1	68.1
4-14	7.3	8.6	28.2
> 15	0.5	2.3	3.7

In 1957, about 12.8 million tons of pulp were made by the kraft process in mills located as shown in Figure 8 in the Appendix. The United States production of pulp by the kraft process from the year 1957 to 1967 is shown in Table 21 in the Appendix.

3.2.4 Coke Ovens

Hydrogen sulfide is produced in the coking operation at the rate of about 6.7 pounds per ton of coal charged.[70] The effluent gas from coke ovens contains about 6,000 to 13,000 μg/m³ of hydrogen sulfide.[107] During cooling and scrubbing, approximately 50 percent of the hydrogen sulfide is removed. The remaining gas is either used as is for firing the coke ovens; purified further (partial desulfurization) and then used for firing of coke ovens; or completely desulfurized and used for municipal gas. The hydrogen sulfide content of nonpurified, partially purified, and municipal gas is shown in Table 9.

TABLE 9

HYDROGEN SULFIDE CONTENT OF COKE-OVEN GAS[107]

Type of Gas	μg/m³
Nonpurified	5,000-13,000
Partially desulfurized	1,500-5,000
Municipal gas or pipeline gas	None

Hydrogen sulfide emissions can occur throughout the complete coking cycle from coke-oven charging to hydrogen sulfide removal (desulfurization).[64] The sources of these emissions, other than charging and discharging emissions, and their causes are shown in Table 10. No data were found on the magnitude of hydrogen sulfide concentration in the atmosphere in or around coke ovens. However, one reference indicated that it is rarely of sufficient magnitude to create problems or evoke complaints from nearby residents.

TABLE 10

SOURCES OF HYDROGEN SULFIDE EMISSIONS IN COKE PLANTS[107]

Source of Emission	Cause of Emission
Condensation	
Unburnt gases escaping from the gas torches	
In normal operation with torch shut off	Leakage at stop valves
With torch open during operational failures	Failure of ignition device
Gases escaping from water seals	Defective seals
Outflow collectors on coolers; collector and separator tanks	Gas escape from liquids
Ammonia Scrubber	
Outflow collectors and collector tanks	Gas escape from washing of fluid
Secondary coolers for primary-cooler outflow (in semi-direct process)	Escape of hydrogen sulfide with the cooling-tower vapors
Benzol Scrubber and Plant	
Outflow receivers of scrubbers and washing oil tanks	Gas escape from washing fluid
Cooler-ventilating lines	Escape of sulfur-containing compounds with low boiling point, together with ventilating gases
Desulfurization of Gas	
Outflow receivers and tanks for scrubbing fluid	Gas escape from washing fluid

In 1966 about 66 million tons of coke were produced in the United States in 66 coke oven plants. The value of the coke at the coke oven was estimated to be $1,144 million. The production rate of coke from 1957 to 1968 is shown in Table 22 in the Appendix.

3.2.5 Mining

Burning coal refuse piles have been a continual cause of air pollution, and one of the combustion products emitted to the atmosphere is hydrogen sulfide.[131] Approximately 20 percent to 50 percent of the raw anthracite processed in cleaning plants is rejected as refuse. At many operations the refuse discarded amounts to about 33 percent of the tonnage produced. This refuse over the years has accumulated in coal refuse piles, some of which contain millions of tons.[125] The piles ignite either through spontaneous combustion, carelessness, or deliberate action. A recent survey indicated that there are approximately 500 burning piles in 15 States.[125]

The hydrogen sulfide generated during combustion disperses into the atmosphere. Significant concentrations of hydrogen sulfide gas have been measured in communities adjacent to burning coal piles. Sussman and Mulhern[131] reported that measurements made in July 1960 adjacent to a large burning anthracite refuse pile showed an hourly maximum average of 600 $\mu g/m^3$. The minimum hourly average was 140 $\mu g/m^3$.

Other possible sources of hydrogen sulfide from mines include underground mine fires and sulfide ore mines. However, no information was found on these sources.

3.2.6 Iron-Steel Industry and Foundries

Small amounts of hydrogen sulfide are given off when blast furnace slag is granulated.[6] Woehlbier and Rengstorff[143] showed experimentally that the amount of hydrogen sulfide formed is proportional to the amount of hydrogen formed during the quenching process. No information was given on the amount of hydrogen sulfide released to the atmosphere by plant granulation operations. Typical hydrogen sulfide exhaust emissions from foundries are 0.002 tons per non-ferrous foundry producing 50 tons of castings per day, and 0.023 tons per gray iron foundry producing 200 tons of castings per day.[69]

3.2.7 Chemical Industry

Hydrogen sulfide is a by-product of many chemical operations. In general, it is formed when sulfur or sulfur compounds are associated with organic materials at a high temperature. For example, it is a by-product in the manufacture of carbon disulfide. The process of producing thiophene by the reaction of sulfur with butane at elevated temperatures also produces hydrogen sulfide.[107]

Other sources of hydrogen sulfide in the chemical industry are the manufacture of sulfur dyes[83] and the production of viscose rayon, ethyl and methyl parathion (pesticides),[128] organic thiophosphate,[86] and many other organic sulfur chemicals. In addition, hydrogen sulfide is evolved from some grease and fatty acid-making processes. Approximately 6 tons of hydrogen sulfide are formed for every 100 tons of viscose rayon produced.[81] Inorganic processes which evolve hydrogen sulfide are zinc smelting and refining,[122] manufacture of barium chloride from barium sulfide, and production of phosphorus compounds, pigments, lithopone, and sodium sulfide.[101] Hydrogen sulfide is also emitted during the manufacture of stove clay and glass.[69,101] The only data found on the magnitude of hydrogen sulfide emissions were 0.024 tons reported per chemical and allied products plant consuming 10^9 BTU per day, and 0.17 tons per cement plant producing 4,830 barrels per day.[69]

Yanysheva[146] measured the hydrogen sulfide concentration in the atmosphere at distances of 200 to 2,500 meters from an electric power plant and chemical combine and up to 800 meters from a phenol production plant. The chemical combine produced sulfuric acid, nitric acid, chlorine, and chlorinated lime. The atmospheric hydrogen sulfide concentration measured varied between 600 and

1,600 μg/m³. Burakhovich[28] reported on hydrogen sulfide measurements made in the vicinity of Lisichansk and Rubezhnoe chemical plants in Russia. The Lisichansk plant manufactures mineral fertilizers, synthetic monomers, ammonia, alcohols, and plastics. The Rubezhnoe plant produces high quality dyes, dye intermediates, and various poisonous chemicals. The atmospheric hydrogen sulfide measurements are shown in Table 11.

Glebova[44] measured the concentration of hydrogen sulfide in the atmosphere at 1 km from a viscose rayon plant. The maximum single concentration was 50 μg/m³. Measurements were also made in the vicinity of the Dorogomelovsk Chemical Manufacture Plant, which produces sulfur dyes and mercaptobenzothiazole rubber accelerators. The hydrogen sulfide concentrations at various distances from the plant are shown in Table 12.

3.2.8 Animal Processing Plants and Tanneries

Hydrogen sulfide is generated in animal processing plants during the decomposition of protein material.[125] Summer[129] reported that hydrogen sulfide and organic sulfur compounds are produced in an offal cooking plant when hooves and horns of cattle and other animals are treated with high-pressure live steam. Hydrogen sulfide is also produced during the cooking of meat. In stale meat, approximately

TABLE 11

HYDROGEN SULFIDE CONCENTRATIONS AT VARIOUS DISTANCES FROM PLANTS[28]

(One-Time Maximum in $\mu g/m^3$)

	Lisichangk Plant		Rubezhnoe Plant			
Year	2,000m	4,000m	500m	1,000m	2,000m	4,000m
1963	40	21				
1964	50		35	64	>8	>8
1965			17	18	15	9

TABLE 12

ATMOSPHERIC AIR POLLUTION BY HYDROGEN SULFIDE AT DIFFERENT DISTANCES FROM SOURCE OF POLLUTION[41]

Distance in Meters	Maximum Concentration ($\mu g/m^3$)	Minimum Concentration ($\mu g/m^3$)
100	66	16
200	58	35
300	59	39
400	40	26
500	35	20
750	26	15
1,000	22	14
1,250	11	05

0.15 pounds of hydrogen sulfide is formed per ton of raw meat at 100°C. Only a trace is formed during the cooking of fresh meat.[129]

During the 1920's and the early thirties, there were many cases of poisoning among tanners (some fatal) mainly caused by hydrogen sulfide.[119] The air concentrations at those times varied from 1,000 to 540,000 $\mu g/m^3$.[119] However, recent results of a nine-year-study on tanneries in Russia showed that the hydrogen sulfide has been almost eliminated in modern tanneries.[119] No information was found on United States tanneries, but it can be assumed that the hydrogen sulfide problem has been largely eliminated.

Other sources of hydrogen sulfide are stockyards, cheese and dairy plants, and wool scrubbing plants.[101] No information was available on emissions from these sources.

3.3 Product Sources

This category is not applicable since hydrogen sulfide is produced only as a by-product.

3.4 Other Sources

3.4.1 Combustion Processes

Hydrogen sulfide is released when coal, oil, or gas is burned. The amount of hydrogen sulfide depends upon the amount of sulfur in the fuel and the efficiency of the combustion process. In an efficient combustion system, the hydrogen sulfide is oxidized to sulfur dioxide. In a study of sulfur released from domestic boilers, it was found that hydrogen sulfide was given off from open fires during heavy smoke emission, mainly just after refueling. The emission factors for fuel combustion are given in Table 13.

TABLE 13

HYDROGEN SULFIDE EMISSION FACTORS

Combustion Source	Emission Factor	Reference
Coal	.0045*/lb coal	110
Fuel oil	1 lb/1,000 lb oil	8,121
Natural gas (density 0.0475)	0.13 lb/1,000 lb gas	8

*lb/sulfur/lb coal.

Hydrogen sulfide is also given off by apartment incinerators and sanitary land fills. Eliassen[37] reported in 1959 on estimates of hydrogen sulfide discharged daily from domestic and municipal sources in a metropolitan area of 100,000 persons. According to this estimate, domestic heating would produce 1,000 pounds of hydrogen sulfide daily from coal combustion, 500 pounds from oil, and 0.1 pounds from gas; apartment incineration would produce 24 pounds daily, and sanitary land fill would produce trace amounts.

3.4.2 Polluted Water

In some localized situations, air pollution due to natural biological processes in polluted waters includes hydrogen sulfide air concentrations that can produce blackening of paint as well as odors above the hydrogen sulfide odor threshold. Denmead[34] reported on the hydrogen sulfide emissions from a shallow tidal inlet in Auckland, New Zealand. This inlet was polluted by untreated domestic sewage and food processing sewage. Surveys conducted during 1957 showed that the average daily concentration of hydrogen sulfide in the air was 380 $\mu g/m^3$. This was computed to represent about 1,500 $\mu g/m^3$ during night hours, a concentration high enough to produce paint-blackening and the foul odor. The problem cleared up when the domestic and food processing wastes were treated in a new sewage treatment plant prior to discharge into the tidal inlet.

A similar incident occurred on the island of Oahu in March 1958 when rainwater filled a natural basin and remained there due to inadequate drainage. The water in the basin destroyed 80 acres of Akulikuli grass growth. The stagnant water caused the plant life to decompose, producing a strong fecal stench. Two weeks later, hydrogen sulfide was quantitatively measured in the air. The hydrogen sulfide was never present in levels dangerous to health, but did cause tarnishing of copper and silver. House paint also was visibly affected. Measurements made at the drainage ditch where water was pumped into a concrete culvert showed hydrogen sulfide concentrations as high as 30,000 μg/m^3. The hydrogen sulfide phase of the pollution lasted for a period of about 10 days.[45]

In Terre Haute, Ind., during late May and early June 1964, the concentrations of hydrogen sulfide in the atmosphere were sufficient to cause public complaints because of paint-blackening and physical discomfort. Atmospheric concentrations exceeding 460 μg/m^3 were measured. The main source of the pollution was found to be a 36-acre industrial lagoon used for biodegradation of organic industrial wastes.[7,123]

3.4.3 Well Water

Another hydrogen sulfide source is municipal plants for removing hydrogen sulfide from well waters. Sheeley *et al.*[117] reported that water aeration plants in the city of Jacksonville, Fla., emit about 0.15 tons per day of hydrogen sulfide. They state that the plants are a particularly troublesome cause of nuisance complaints.

3.4.4 Sewage Plants and Sewers

Hydrogen sulfide is produced biologically in sewers from organic compounds formed by hydrolysis of materials like cystine and methionine and by reduction of sulfates. Sewage usually contains 1 to 5 ppm of organic sulfur compounds, while some industrial wastes, such as from wool, contain as high as 50 to 100 ppm.[90] Sulfates are present in sewage almost entirely as inorganic sulfates and enter the system in waste water, saline ground water, or through industry discharge of tidal or sea water to sewers. The factors that influence hydrogen sulfide generation in sewers include sewage temperature, content of sewage, velocity of flow, age of sewage, pH value of sewage, sulfate concentration, and ventilation of the sewer. Hydrogen sulfide is also generated and released from sewage treatment plants.[77] The hydrogen sulfide is formed in digesters during anaerobic digestion of the sewage sludge and industrial wastes.[90] Atmospheric measurements made at a sewage treatment plant in El Paso, Tex., in 1958 showed that the hydrogen sulfide concentration varied between 24 $\mu g/m^3$ and 2,120 $\mu g/m^3$, with the average concentration 610 $\mu g/m^3$. At a sampling station 100 yards from the sewage plant, the maximum hydrogen sulfide concentration was 205 $\mu g/m^3$.[55]

3.5 Environmental Air Concentrations

Routine measurements of the concentration of hydrogen sulfide in the environmental air are not made by the National Air Sampling Network. Data from selected areas for various time periods indicate average levels of hydrogen sulfide in the atmosphere of 1 to 92 $\mu g/m^3$, as indicated in Table 14.

TABLE 14

ATMOSPHERIC HYDROGEN SULFIDE CONCENTRATIONS ($\mu g/m^3$)

Location	Average	Maximum	Ref.
New York City			
1956-61	1	13	81
1962	1	6	13
Elizabeth, N. J. Aug.-Oct. 1963	1	247	81
Hamilton Township, N. J. May-Oct. 1962	1	49	81
Woodbridge Township, N. J. April-May 1961	1	305	81
Greater Johnstown Area, Pa. 1963	3	210	47
Winston-Salem, N. C. Nov.-Dec. 1962	3	011	85
Lewiston-Clarkston Area, North Lewiston, Idaho, near pulp mill, 1962		37	1
Great Kanawha-River Valley Industrial Area Feb. 1950-Aug. 1951	3-92	410	16
Camas, Wash. 1962	0-1	6	8
Santa Barbara, Calif. 1949-1954		1,400	58
St. Louis, Mo. 1964	2-6	94	39
Terre Haute, Ind. May-June 1964		>460	7

4. ABATEMENT

A number of systems and types of equipment have been developed for removal of hydrogen sulfide from gas streams. Many of these systems are designed to recover the hydrogen sulfide for subsequent conversion to valuable by-products, such as sulfur and sulfuric acid. Many of the removal systems are based on scrubbing the gas streams with a suitable absorbent and then removing the absorbed gas from the absorbent for disposal by burning or conversion to a valuable by-product. Some of the absorbents convert the hydrogen sulfide to an innocuous compound which may be useful in some cases as a fertilizer. Such chemicals as aqueous solutions of diethanolamine and monoethanolamine, sodium hydroxide, tri-potassium phosphate, and aqueous solutions of chlorine and sodium carbonate have been used as absorbents. Different types of contacting devices (wet scrubbers) have been used, including conventional and novel design spray towers, plate towers, and venturi scrubbers.

4.1 Kraft Paper Mills

In kraft paper mills, the greatest reduction of hydrogen sulfide emissions was achieved by the black liquor oxidation process. This process consists of oxidizing the sulfides in the weak black liquor (before the multiple-effect evaporation) or strong black liquor (after the multiple-effect evaporation) by contacting it with air in a packed-tower, thin-film, or porcus-plate black liquor oxidizing unit.

The oxidation converts the sulfides to less volatile compounds which are also less odorous and have less tendency to escape.[68] This conversion has the effect of reducing the hydrogen sulfide emissions from the direct-contact evaporator and the recovery-furnace stack by 80 to 95 percent.[51,68,74] Since these evaporators and furnace stacks are the principal emitters of hydrogen sulfide in kraft mills,[101] the net result is a substantial reduction of hydrogen sulfide emission. The weak black liquor oxidizing process also reduces emission from the multiple-effect evaporators.

The majority of the black liquor oxidizing systems installed in the United States are based on oxidation of weak liquor, and are located in the Western part of the country. In the Southern part of the country, the woods used in kraft processes cause excessive foaming problems in the weak black liquor oxidizing process.[74,96] To alleviate this, a few Southern mills have installed a process based on oxidizing the strong black liquor.[96,97]

The key to minimizing hydrogen sulfide emissions from the recovery furnace, even in those systems employing black liquor oxidizing systems, is proper furnace-operating conditions.[51] From Figure 5 in Section 3.2.3, it can be seen that at furnace loading greater than design capacity, hydrogen sulfide emissions rise substantially. For minimum emissions from the recovery furnace, the furnace should not be operated above design conditions. There should be 2 to 4 percent excess oxygen leaving the secondary burning zone (i.e., leaving the furnace), and there should be adequate mixing (turbulence) in the secondary combustion zone.

In the direct-contact evaporator, where the flue gases from the recovery furnace are used to concentrate the black liquor, the carbon dioxide in the flue gases reacts with the sulfite in the black liquor to release hydrogen sulfide.[96] Even where the black liquor oxidizing process is employed, some sulfite remains after oxidation. This releases some hydrogen sulfide when contacted with flue gases. Therefore, removal of the direct-contact evaporator from the stream further reduces sulfide emissions.

In the Scandinavian countries the recovery furnaces are designed and operated in such a manner that black liquor can be fed directly to them from the multiple-effect evaporators. These furnaces efficiently burn all malodorous compounds; the necessity for oxidizing black liquor prior to burning is therefore eliminated. Approximately 45 mills in Sweden use additional multi-effect evaporators to replace the direct-contact evaporator and burn unoxidized black liquor.[32] Three such installations are being installed in North America.[32] The exact location of these units was not specified.

Another approach to burning unoxidized black liquor while still minimizing the emission of malodorous compounds was described by Hochmutch.[53] In this system, the combustion gases from the recovery furnace are used to preheat air in a recuperative air preheater. The hot air is then used to concentrate the black liquor in the direct-contact evaporator. The air from the direct-contact evaporator is then used as primary and secondary air in the recovery furnace, where malodorous compounds in the air are incinerated in the high-temperature combustion zones.

To reduce recovery-furnace particulate emissions, some mills have installed a secondary wet scrubber to follow the primary scrubber (direct-contact evaporator). Secondary scrubbing does not remove hydrogen sulfide unless a basic solution such as weak caustic is used. Limited pilot plant studies and some plant experience have shown that weak wash (i.e., weak caustic solution) has removed hydrogen sulfide from the stack gases. In other instances, no hydrogen sulfide removal has been obtained under such a system. In general, the removal of hydrogen sulfide from flue gases containing 11 to 14 percent carbon dioxide with a caustic solution has not been developed.[23,24,26,74]

Other sources of hydrogen sulfide emissions from kraft mills are the noncondensible gases released from digesters and multiple-effect evaporators. Various systems developed and installed for minimizing these emissions are generally based on collecting the noncondensible gases in a gas holder, then oxidizing or burning them at a constant flow rate. The various methods used are the following:

(1) Burning the gases in the recovery furnace or lime kiln.[116]

(2) Oxidizing the gases in a separate catalytic oxidizing furnace or a direct-flame incinerator.[74, 114]

(3) Oxidizing the gases in an absorption tower with aqueous chlorine solutions, such as chlorine bleach water from the bleach plant, waste chlorine, hypochlorite, etc. Sometimes this is followed by processing in another absorption tower, where the absorbent is either a weak chlorine solution or a caustic solution.[61, 116, 141]

(4) Absorbing the gases with a caustic solution in a scrubber.[61]

In the lime kiln, the use of wet scrubbers with an alkaline-absorbent, efficient control of combustion, and proper washing of lime mud will substantially reduce hydrogen sulfide emissions. Scrubbing smelt tank gaseous emissions with weak wash or green liquor in an absorption tower will reduce hydrogen sulfide emissions from this source.[116]

Around 1951, masking of odors by adding aromatic compounds to the digester, the black liquor, and the stack gases was tried in the United States. This strictly makeshift approach did not solve the basic pollution problem and is not used at the present time.[141]

4.2 Petroleum Industry and Petrochemical Plants

In refineries and petrochemical plants, small quantities of hydrogen sulfide associated with gas streams can be burned in the plant full system or in a flare.[88] In refineries and natural gas plants where larger quantities of hydrogen sulfide are associated with gas streams (sour gas), the hydrogen sulfide is generally extracted in an absorption tower using a number of different absorbents, such as aqueous amines (Girbatol process); sulfalone (Shell process); alkaline arsenites and arsenates (Giammarco-Vetrocoke process); organic solvents such as propylene carbonate, glyceral triacetate, lutoxy-dethylene-glycol acetate, methoxy-triethylene glycol acetate (Fluor solvent process); and many others. These processes are regenerative--that is, the absorbent is regenerated by removing the hydrogen sulfide and reused. In the case of the Giammarco-Vetrocoke process, sulfur is recovered directly as part of the absorbent regeneration process. In the other processes the hydrogen sulfide from the regeneration process is converted to sulfur by the Claus process.[38,79,91] The sulfur can be further processed into sulfuric acid if this is the end product desired.

4.3 Coke-Oven Plants and Chemical Plants

In coke-oven plants, the coke-oven gases are often purified of hydrogen sulfide by passing the gases through iron-oxide-impregnated wood shavings.[11,38,126] This process is generally nonregenerative, although methods for regenerating the iron oxide have recently been developed.[80] Regenerative liquid absorption systems using such absorbents as ammonium carbonate, sodium thioarsenate, and sodium arsenate solutions have also been used.[38,42] Similarly, various liquid absorbents have been used in the chemical industry for removal of hydrogen sulfide in gas streams. For example, hydrogen sulfide liberated in the production of sulfur dyes in aniline plants is effectively absorbed by alkali in scrubbers.[83] Another commonly used method for preventing release of hydrogen sulfide to the atmosphere in the chemical industry is to collect the various gaseous vents and destroy them by incineration.[128]

4.4 Coal Piles

The pollution of the atmosphere in the vicinity of burning coal refuse piles can be minimized by constructing the refuse piles in such a manner that ignition is minimized and it is possible to easily extinguish a fire.[131]

4.5 Tanneries

In the tanning industry, practices adopted in modern tanneries in Russia have essentially eliminated the hydrogen sulfide problem. These consist of more rapid processing of raw material, use of lime solutions to destroy hide proteins and alkalize sodium sulfide, and neutralization of the semimanufactured products to eliminate residual sodium sulfide which previously contaminated acid-tanning solutions.[119]

4.6 Sewers and Sewage Plants

In sewage plants, the most comprehensive elimination of hydrogen sulfide is accomplished by enclosing the process and venting the gases to an incinerator.[77] Other methods of removing hydrogen sulfide are absorbing or chemically oxidizing the gas. The oxidation process is utilized in New York City and Sarasota, Fla.[77] Other methods consist of odor-masking with scented mint, catalytic combustion, and odor counteraction.[77]

In sewers, the production and release to the atmosphere of hydrogen sulfide can be minimized by maintaining sufficient velocities of sewage to avoid sulfide buildup and minimizing lines of pressure and points of high turbulence. Atmospheric pollutions may also be controlled by adequate ventilation, injection of air to maintain aeration conditions, cleaning of sewers to remove slime and silt, use of chemicals such as chlorine and ozone for suppressing biological activity,[90] and addition of specific biological life to suppress the development of organisms producing the hydrogen sulfide.[114] A method of preventing release of hydrogen sulfide to the atmosphere which has had some degree of success is trapping the gas in laterals, branches, and mains by use of specially designed junctions.[114] A method utilized by the County Sanitation District of

Los Angeles to control hydrogen sulfide is to add lime slurry to sewage periodically in relatively large quantities.[114]

4.7 General Abatement Systems

Kalyuzhnyi et al.[63] reported that reduction of hydrogen sulfide and other pollutants in air was achieved by placing a green vegetation belt between the industrial emitter and the residential areas. They observed that hydrogen sulfide concentrations outside the green belt then decreased from 70 $\mu g/m^3$ to 30 $\mu g/m^3$ at 500 meters, while inside the green belt the hydrogen sulfide concentrations decreased from 70 $\mu g/m^3$ to 25 $\mu g/m^3$; this difference was considered significant by the author.

5. ECONOMICS

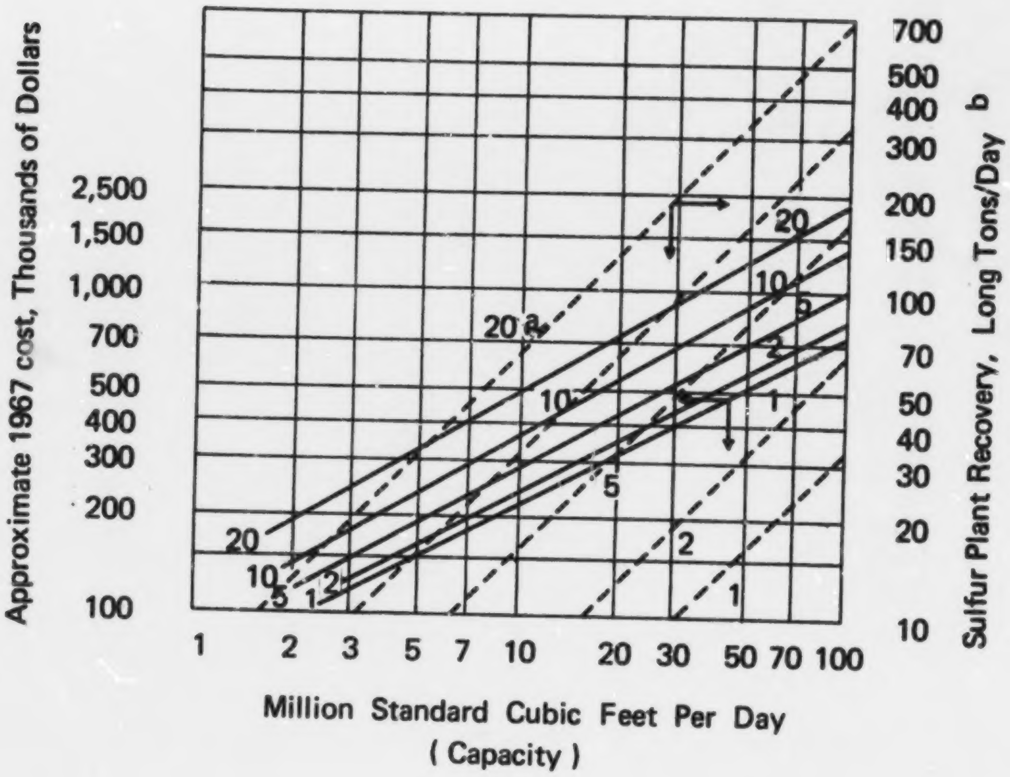
Incidents in which hydrogen sulfide caused metal-tarnishing and paint-blackening have been reported in areas adjacent to kraft paper mills, industrial waste lagoons, and water aeration plants, as outlined in the section on Effects. In one instance in Terre Haute, Ind., effects on health were reported. However, few persons sought medical attention. The economic inpact of the losses was not reported. The major economic effect of hydrogen sulfide pollution on the general public is the nuisance effect (due to the foul smell), with the resultant decrease in property values in areas adjacent to emitters. No information was available on the value of property in a hydrogen sulfide-polluted area in relation to an area not polluted by hydrogen sulfide.

Tarnishing of metals has necessitated the use of gold in electrical contacts instead of silver, which is sensitive to hydrogen sulfide corrosion. It has been estimated that if silver could be used instead, in 1963 a savings of approximately $14.8 million could have been realized.[67]

In cases of severe hydrogen sulfide pollution, the economic inpact is substantial. For instance, in Poza Rica, Mexico, 22 people died, 320 persons were hospitalized, and 100 percent of the canaries and 50 percent of the livestock and domestic animals died. However, no information was found on the magnitude of the cost to residents of the area.

Major expenditures have been made in kraft plants, natural gas plants, coke-oven plants, and chemical plants to minimize the release of hydrogen sulfide and other odor-producing sulfur compounds to the atmosphere. However, no studies were found on the total dollar value of abatement equipment or systems or their operation. The pulp and paper industry has spent $75 million to date to control air emissions. This includes $40 million spent over the last four years. In the next four years the industry expects to spend $60 million. The cost includes the amounts spent for all phases of air pollution, including process changes in kraft mills.[40] The percent of the total expenditure associated with hydrogen sulfide abatement is not known.

Major expenditures have been made by refineries and natural gas plants to remove hydrogen sulfide from sour gases and to recover the sulfur. The cost of desulfurization plants and sulfur-recovery plants is shown in Figure 6 and Figure 7. However, the value of the sulfur recovered generally exceeds the cost of construction and operation of the facilities required to recover it. Data on the production of hydrogen sulfide are presented in Section 3.



Key

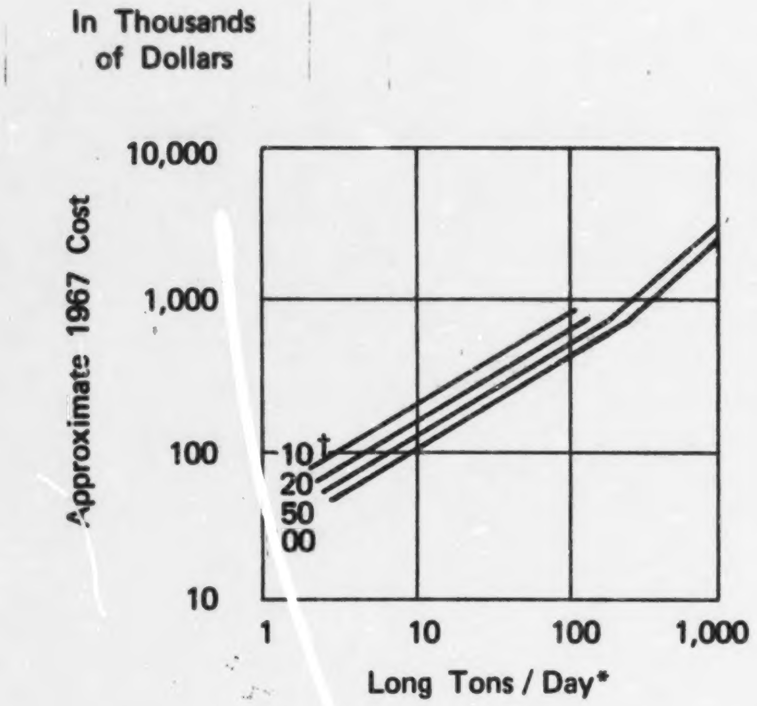
—— Approximate 1967 cost.

---- b Sulfur plant recovery, based on 96% recovery of hydrogen sulfide, and 90% recovery of sulfur in sulfur plant.

1 - 20 a Hydrogen sulfide in gas, % .

FIGURE 6

Approximate Cost of Gas Desulfurization Plants in 1967[92]
(amine or other types)



* Product capacity based on:

Hydrogen Sulfide in Sour Gas, %	% Sulfur Recovery in Sulfur Plant
10	89
20	91
50	93
100	95

† % Hydrogen Sulfide in gas.

FIGURE 7

Sulfur-Recovery Plant Investment[48]

6. METHODS OF ANALYSIS

The methods used in air pollution studies for hydrogen sulfide analysis are mainly based on iodometric methods such as titrating with iodine, methylene blue methods, molybdenum blue methods, and various modifications of the lead acetate paper and tile methods. The methylene blue method is based on precipitating cadmium sulfide from alkaline suspension of cadmium hydroxide by hydrogen sulfide in a known air sample. The alkaline suspension of cadmium hydroxide is contained in a standard impinger (0-1 CFM), through which is drawn the sample of air to be analyzed. The sulfide ion is then reacted with a mixture of p-amino-dimethyl-aniline, ferric ion, and chloride ion (ferric chloride) to yield methylene blue. The concentration of hydrogen sulfide is then determined optically by a colorimeter or spectrophotometer.[59,60,124] This method is good for hydrogen sulfide determinations down to the $\mu g/m^3$ range. Lahmann and Prescher[73] found that the cadmium sulfide suspensions are unstable at low concentrations and are decomposed by light. From tests run on samples of air containing from 7 to 170 $\mu g/m^3$, they concluded that the method of sampling (i.e., amount of light which penetrates the sample) will affect the analytical results. Recently Bamberger and Adams[18] claimed to have minimized these problems by adding arabinogalactan, avoiding exposure to light, and analyzing the samples as soon as possible after collection. By this procedure they claim a sensitivity of a few ppb of hydrogen sulfide in a 240 liter sample taken over a 2-hour period. This improvement gives about an 80 percent recovery of hydrogen sulfide.

Variations on the methylene blue method include the absorption of the hydrogen sulfide in zinc acetate instead of the cadmium salts. However, this variation is not as accurate as the cadmium salt method because zinc acetate loses hydrogen sulfide during sampling by air stripping and aging if allowed to stand for more than 2 hours. In addition, the collection efficiency for cadmium hydroxide is reported to be higher than for zinc acetate.[52]

The molybdenum blue method is based on absorbing the hydrogen sulfide from the air sample in an acid solution of ammonium molybdate. The color developed in the ammonium molybdate by the hydrogen sulfide is determined optically by a colorimeter.[27,112]

The cadmium sulfide method is an example of the iodometric methods for determining hydrogen sulfide concentration in air. A known quantity of air is passed through two bubblers in series containing ammoniacal cadmium chloride solution. The collected samples are then stripped of any trapped sulfur dioxide, and the cadmium sulfide precipitate is dissolved in concentrated hydrochloric acid. The solution is then titrated with iodine using starch as the indicator. The hydrogen sulfide concentration in the air can be calculated from the amount of iodine added. Other cadmium solutions--cadmium acetate, for example--can be used as the absorbing solution.[59] This method is accurate to about 700 $\mu g/m^3$ for a 30-liter air sample.[59]

The spot method using paper or tiles impregnated with lead acetate has been widely used to measure low concentrations of hydrogen sulfide in the atmosphere. The tiles are preferred in air pollution work. The unglazed tiles are impregnated with lead acetate and exposed in a place where they will be protected from rain. After exposure, the shade of the tiles is compared with known standards to estimate the concentration of hydrogen sulfide. In general, this method does not give accurate quantitative results, but rather, an indication of relative exposures of various localities to hydrogen sulfide.[59,124] Gilardi and Manganelli[43] did experimental studies on the light absorbence of lead acetate-impregnated tile surfaces after exposure to various concentrations of hydrogen sulfide to develop an accurate quantitative measurement technique. From their experiments they concluded the following:

(1) Exposure unit $(\frac{mg\text{-}hr}{m^3})$ is a useful parameter in representing hydrogen sulfide exposure.

(2) Average concentrations of hydrogen sulfide between 150 and 1,500 $\mu g/m^3$ can be determined by the measurement of surface absorbency of lead acetate.

(3) Fading of darkened tiles is accelerated by air turbulence and light.

Chiarenzelli and Joba[30] also found that the tiles faded on standing and that oxidation products formed. From these facts they concluded that the lead acetate tile method is unsatisfactory for periods greater than a day or two.

Automatic tape samplers based on lead acetate-impregnated filter paper have been developed for field air pollution application which continuously measure the hydrogen sulfide content of the atmosphere. The AISI or Hemeon tape sampler draws a known quantity of air through lead acetate-impregnated filter paper. If hydrogen sulfide is present in the atmosphere, a dark spot is formed which is measured by determining the optical density of the spots as compared to a standard.[36] Sanderson, Thomas, and Katz[113] reported that field experience has shown that large measurement errors can occur due to fading of the color of the precipitated lead sulfide spots by action of light, sulfur dioxide, ozone, or any other substance capable of oxidizing lead sulfide. This fading may even occur during the sampling period. The fading can occur in a short time and a negative result is therefore not indicative of the absence of hydrogen sulfide.[113] Other factors that affect the accuracy of the AISI tape sampler are relative humidity of the air and the consistency of absorbence of the blank paper.[113] On the positive side, High and Horstman[52] reported obtaining results with the AISI tape sampler that were in reasonably good agreement with results obtained by the methylene blue method. They stated that the lead sulfide stains produced on the lead acetate filter paper did not fade significantly during an 8-week storage period when stored in vapor- and moistureproof bags.

Pare[98] suggested that mercuric chloride-impregnated filter paper be used in tape sampler paper as an improvement over the lead acetate-impregnated paper. He reported that the mercuric chloride paper tape is sensitive and reliable for determination of hydrogen sulfide in air and the spots are stable even in the presence of high levels of ozone, nitrogen oxides, and sulfur dioxide. He stated that it provided an adequate sensitivity on the order of 700 $\mu g/m^3$. Dubois and Monkman[36] reported that although the spots formed by hydrogen sulfide on the mercuric chloride tape are resistant to fading effects, sulfur dioxide in the air results in a substantial change in hydrogen sulfide threshold of the tape.

Falgout and Harding[38] reported a method based on drawing air through a silver membrane filter. The hydrogen sulfide reacts to form silver sulfide, which results in a decrease in the reflectance of the silver surface. The reflectance of the membrane is measured before and after exposure, and the decrease in reflectance is proportional to the hydrogen sulfide exposure. This method is also sensitive to mercaptans in the air. Other methods have been used whereby silver coupons or coupons coated with lead-base paint are exposed to air. The sulfide formed is removed and analyzed by the methylene blue method. Silver tarnishing of coupons as measured by light reflectance has also been used as a tool for measuring relative concentrations of hydrogen sulfide at various locations.[52] Detector tubes containing inert particles coated with silver cyanide or lead acetate have been developed for testing for hydrogen sulfide.[111] The sensitivity of this method is 0.04 μg with a detection limit of 140 $\mu g/m^3$.

Gas chromatographs with minimum detection threshold for hydrogen sulfide of 150 $\mu g/m^3$ have been used in air pollution and industrial work.[14,82] Adams and Koppe[2] determined that with a gas chromatograph, the bromine microcoulometric titration cell had the greatest potential for sulfur-specific analysis at a sensitivity required for direct analysis of small-volume samples. Hydrogen sulfide concentrations in the range of 15 μg/m^3 to 1,200,000 μg/m^3 can be measured by an electrolytic titrator which is preceded by a gas scrubber train to remove interfering sulfur compounds.[133] Lahmann[72] reported that a sensitive new instrument based on galvanic measuring cells has been developed in Germany for measuring the hydrogen sulfide content of air.

7. SUMMARY AND CONCLUSIONS

Hydrogen sulfide is highly toxic to humans, and at concentrations over 1,000,000 $\mu g/m^3$ quickly causes death by paralysis of the respiratory system. At lower concentrations, hydrogen sulfide may cause conjunctivitis with reddening and lachrymal secretion, respiratory tract irritation, psychic changes, pulmonary edema, damaged heart muscle, disturbed equilibrium, nerve paralysis, spasms, unconsciousness, and circulatory collapse.

The odor threshold for hydrogen sulfide lies between 1 and 45 $\mu g/m^3$. Above this threshold value, the gas gives off an obnoxious odor of rotten eggs, which acts as a sensitive indicator of its presence. At these concentrations, no serious health effects are known to occur. At 500 $\mu g/m^3$, the odor is distinct; at 30,000 to 50,000 $\mu g/m^3$ the odor is strong, but not intolerable; at 320,000 $\mu g/m^3$, the odor loses some of its pungency, probably due to paralysis of the olfactory nerves. At concentrations over 1,120,000 $\mu g/m^3$, there is little sensation of odor and death can occur rapidly. Therefore, this dulling of the sense of smell constitutes a major danger to persons exposed to high concentrations of hydrogen sulfide.

Hydrogen sulfide produces the same health effects on domestic animals as on man, and at approximately the same concentrations.

An episode occurred at Poza Rica, Mexico, where the accidental release of hydrogen sulfide from a natural gas plant killed 22 persons, hospitalized 320 people and killed 50 percent of the commercial and domestic animals and all the canaries in the area. No measurements were made of the environmental hydrogen sulfide concentrations at the time of the episode. In Terre Haute, Ind., hydrogen sulfide emanations from an industrial waste lagoon caused foul odor, public complaints, and discomfort. However, very few people sought medical attention. Hydrogen sulfide concentration in the atmosphere during the episode ranged between 34 and 450 $\mu g/m^3$.

There is little evidence that significant injury to field crops occurs at hydrogen sulfide concentrations below 60,000 $\mu g/m^3$. At higher concentrations, the hydrogen sulfide injures the younger plant leaves first, then middle-aged or older ones.

Hydrogen sulfide combines with heavy metals in paints to form a precipitate which darkens or discolors the paint surface. Air concentrations as low as 75 $\mu g/m^3$ have darkened paint after a few hours' exposure. White-lead paints often fade in the absence of hydrogen sulfide due to oxidation of the sulfite to sulfate. Paint darkening has occurred in Jacksonville, Fla., New York City, South Brunswick, N.J., Terre Haute, Ind., and in the areas near Lewiston, Idaho, and Clarkston, Wash. Hydrogen sulfide will also tarnish silver and copper. The sulfide coating formed on copper and silver electrical contacts can increase contact resistance and even weld the contacts shut.

The States of California, Missouri, Montana, New York, Pennsylvania, and Texas have ambient air quality standards. The standards vary from a level of 150 $\mu g/m^3$ averaged over 1 hour in California to a 24-hour average of 7.5 $\mu g/m^3$ for Pennsylvania.

Hydrogen sulfide is produced naturally by biological decay of protein material, mainly in stagnant or insufficiently aerated water such as swamps and polluted water. The background air concentration due to this source is estimated to be between 0.15 and 0.46 $\mu g/m^3$. Industrial emitters of hydrogen sulfide are refineries, kraft paper mills, coke-oven plants, natural gas plants, chemical plants manufacturing sulfur-containing chemicals, viscose rayon plants, food processing plants, and tanneries. The emission of hydrogen sulfide and other organic sulfides--the cause of the foul odor in the vicinity of kraft paper mills--is the major kraft paper mill air pollution problem.

The average concentrations of hydrogen sulfide in the urban atmosphere vary from undetectable amounts to

92 $\mu g/m^3$ (based on limited data). However, measurements as high as 1,400 $\mu g/m^3$ have been recorded, but these have generally been in the vicinity of high hydrogen sulfide emissions.

The largest reduction in hydrogen sulfide emission from kraft mills was achieved by the addition of the black liquor oxidation process to the chemical recovery system. In addition, hydrogen sulfide emissions can be minimized if 2 to 4 percent excess oxygen is maintained in recovery-furnace flue gas, if the furnace is not operated above design conditions, and if noncondensible gases from the digesters and multiple-effect evaporators are scrubbed in a wet scrubber using weak caustic or chlorine water or are incinerated.

In refineries and natural gas plants, the hydrogen sulfide associated with sour gas stream is generally extracted in an absorption tower using absorbents such as aqueous amines. The hydrogen sulfide is recovered from the absorbent and in most cases further processed to produce valuable products such as sulfur or sulfuric acid.

The hydrogen sulfide associated with coke-oven gases is often removed by iron oxide-impregnated wood shavings. Liquid scrubbers using ammonium carbonate and sodium arsenate solutions can also be used. In chemical plants, liquid scrubbers and incinerators are used to minimize hydrogen sulfide emissions.

Proper design, cleaning, and aeration of sewers can minimize emissions of hydrogen sulfides. The most effective method of eliminating emissions of this material from sewage plants is to enclose the process and vent the gases formed to an incinerator.

No information has been found on the economic costs of hydrogen sulfide air pollution or on the costs of its abatement.

The primary methods used in air pollution studies for analyzing hydrogen sulfide are based on iodometric methods (cadmium sulfide method), methylene blue method, molybdenum blue method, and various modifications of the lead acetate paper and tile methods. The automatic tape samplers based on the lead acetate paper method have been developed for field air pollution application. However, there is evidence that the spot formed on the lead acetate tape fades in the presence of oxidants, producing measurement errors. To solve this problem, mercuric chloride-impregnated tape has been developed for use in automatic tape samplers.

Based on the material presented in this report, further studies are suggested in the following areas:

(1) Determine whether continuous exposure to low concentrations of hydrogen sulfide is harmful to health.

(2) Survey all hydrogen sulfide emitters and the magnitude of the emissions from them.

(3) Develop an improved, simple, accurate method for field analysis.

(4) Determine the effectiveness of existing abatement systems at kraft mills and develop more effective systems which will essentially eliminate hydrogen sulfide emissions from kraft mills.

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APPENDIX

TABLE 15

EFFECTS OF HYDROGEN SULFIDE ON HUMANS[41,49,101,102,140]

Concentration ($\mu g/m^3$)	Effects
1-45	Odor threshold. No reported injury to health
10	Threshold of reflex effect on eye sensitivity to light
150	Smell slightly perceptible
500	Smell definitely perceptible
15,000	Minimum concentration causing eye irritation
30,000	Maximum allowable occupational exposure for 8 hours (ACGIH Tolerance Limit)
30,000-60,000	Strongly perceptible but not intolerable smell. Minimum concentration causing lung irritation
150,000	Olfactory fatigue in 2-15 minutes; irritation of eyes and respiratory tract after 1 hour; death in 8 to 48 hrs
270,000-480,000	No serious damage for 1 hour but intense local irritation; eye irritation in 6 to 8 minutes
640,000-1,120,000	Dangerous concentration after 30 minutes or less
900,000	Fatal in 30 minutes
1,160,000-1,370,000	Rapid unconsciousness, respiration arrest, and death, possibly without odor sensation
1,500,000+	Immediate unconsciousness and rapid death

TABLE 16

TIME REQUIRED FOR 50 PERCENT MORTALITY OF SUBJECTS TREATED WITH HYDROGEN SULFIDE [66]
(In Minutes)

Subject	Number Studied	H_2S Concentration (in μg/m^3)			
		1,500,000	380,000	96,000	24,000
Flies	250	7	>960		
Mice	4	18	410	804	>960
Rats	8	14	>960	>960	>960

TABLE 17

TYPICAL GROSS FINDINGS AT AUTOPSY OF RATS AND MICE WHICH DIED DURING EXPOSURE TO HYDROGEN SULFIDE[139]

	Concentration of Hydrogen Sulfide Gas (in $\mu g/m^3$)					
	1,500,000		380,000		96,000	
Organ	Rats (8)	Mice(4)	Rats (8)	Mice (4)	Rats (8)	Mice (4)
Brain	Very slightly congested		Congested	Slightly congested	Congested	Congested
Trachea	Natural	Same as rats	Natural	Natural	Natural	Natural
Lungs	Well collapsed, dark pink, cut surface wet, rare small hemorrhages	Same as rats	Partly distended, extremely hemorrhagic	Massive hemorrhages of all lobes	One-half collapsed, many small hemorrhages	Deep red, apparently massive hemorrhage
Heart	In systole, atria dilated, blood fluid	Same as rats	Distended	Moderate dilatation of right side	Moderate dilatation of right side	Moderately dilated
Liver	Much congested	Same as rats	Congested	Moderately enlarged, very pale, lobules not exaggerated	Medium dark red	Pale, nutmeg color, large
Gall bladder	Not distended	Same as rats	Not distended	Definitely but moderately distended	Not distended	Not distended to moderately distended

TABLE 17 (Continued)

TYPICAL GROSS FINDINGS AT AUTOPSY OF RATS AND MICE WHICH DIED DURING EXPOSURE TO HYDROGEN SULFIDE

Organ	Concentration of Hydrogen Sulfide Gas (in $\mu g/m^3$)					
	1,500,000		380,000		96,000	
	Rats (8)	Mice(4)	Rats (8)	Mice (4)	Rats (8)	Mice (4)
Stomach	Moderately to greatly distended, few small hemorrhages	Same as rats	Distended, few small hemorrhages	Definitely but moderately distended, rare minute hemorrhages	Definitely but moderately distended, moderate number of small hemorrhages	Moderately distended, few hemorrhages of moderate size
Intestines	Natural or with a few small hemorrhages	Same as rats	Large, partly distended	Small intestine slightly distended	Cecum moderately distended	Duodenum dilated
Adrenals	Natural, pink	Same as rats	Pink	Pale	Natural	Natural
Kidneys	Much congested	Moderately congested	Congested	Pale	Medium dark red	Pale

TABLE 18

PERCENTAGE OF LEAF AREA MARKED BY HYDROGEN SULFIDE[20]
(Four-Hour Fumigations)

Plant	Concentration of Hydrogen Sulfide					
	750,000 μg/m³			150,000 μg/m³		
	3 wk[a] Moist[b]	6 wk[a] Moist[b]	6 wk[a] Dry[b]	3 wk[a] Moist[b]	6 wk[a] Moist[b]	6 wk[a] Dry[b]
Lamb's-quarters	100	69	100	53	100	28
Nettle-leaf goosefoot	91	54	83	64	88	24
Chickweed	100	55	88	41	34	29
Dandelion	75	45	76	16	26	13
Sunflower	53	45	78	28	26	17
Kentucky bluegrass	70	28	77	21	18	16
Pigweed	52	31	53	12	23	32
Annual bluegrass	66	18	64	17	9	7
Mustard	52	20	65	16	13	11
Cheeseweed	32	34	53	10	10	3

[a] Age of plants.
[b] Soil condition.

TABLE 19

RELATIVE SENSITIVITY OF PLANTS TO HYDROGEN SULFIDE[20]

Sensitive	Intermediate	Resistant
Lamb's-quarters	Dandelion	Annual bluegrass
Nettle-leaf goosefoot	Sunflower	Mustard
Chickweed	Kentucky bluegrass	Cheeseweed
	Pigweed	

APPENDIX

TABLE 20

CRUDE OIL CAPACITY IN THE UNITED STATES AS OF JANUARY 1969[130]

State	No. Plants	Crude Capacity[a]	
		b/cd[b]	b/sd[c]
Alabama	6	34,620	36,820
Alaska	1	20,000	21,000
Arkansas	6	93,500	94,985
California	32	1,529,075	1,606,985
Colorado	4	42,900	46,235
Delaware	1	140,000	150,000
Florida	1	3,100	3,150
Georgia	2	9,500	11,000
Hawaii	1	35,000	NR
Illinois	11	704,100	732,300
Indiana	10	565,700	588,800
Kansas	12	389,300	407,300
Kentucky	3	128,500	132,600
Louisiana	16	1,190,850	1,230,000
Maryland	2	19,400	20,500
Michigan	8	146,050	152,000
Minnesota	3	138,300	144,000
Mississippi	4	168,700	181,500
Missouri	1	83,000	84,700
Montana	9	128,200	137,500
Nebraska	1	4,000	4,500
New Jersey	6	523,500	555,000
New Mexico	6	42,610	44,400
New York	2	76,900	81,000
North Dakota	2	55,000	57,000
Ohio	11	491,600	525,900
Oklahoma	14	449,367	464,250
Oregon	1	11,000	12,000
Pennsylvania	13	628,920	659,100
Rhode Island	1	7,500	10,000
Tennessee	1	28,500	29,750
Texas	47	3,118,250	3,244,300
Utah	5	11,950	116,400
Virginia	1	43,600	45,000
Washington	6	219,000	226,000
West Virginia	2	8,570	9,100
Wisconsin	2	29,500	30,600
Wyoming	9	132,900	146,686
Total	263	11,522,512	12,079,201

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[a] State totals include figures converted to calendar-day or stream-day basis.

[b] b/cd = barrels per calendar day.

[c] b/sd = barrels per stream-day.

APPENDIX

TABLE 21

KRAFT PULP PRODUCTION IN THE UNITED STATES[105]

Year	Million Tons/Year
1957	12.8
1958	13.1
1959	14.9
1960	15.3
1961	16.1
1962	17.4
1963	18.7
1964	20.4
1965	22.3
1966	24.4
1967	23.9

APPENDIX

TABLE 22

UNITED STATES COKE PRODUCTION[89]

Year	Tons/Year	Number of Oven Slots
1957-59	60.5×10^6	15,993
1964	60.9×10^6	14,639
1965	65.2×10^6	14,357
1966	66.0×10^6	14,720

APPENDIX

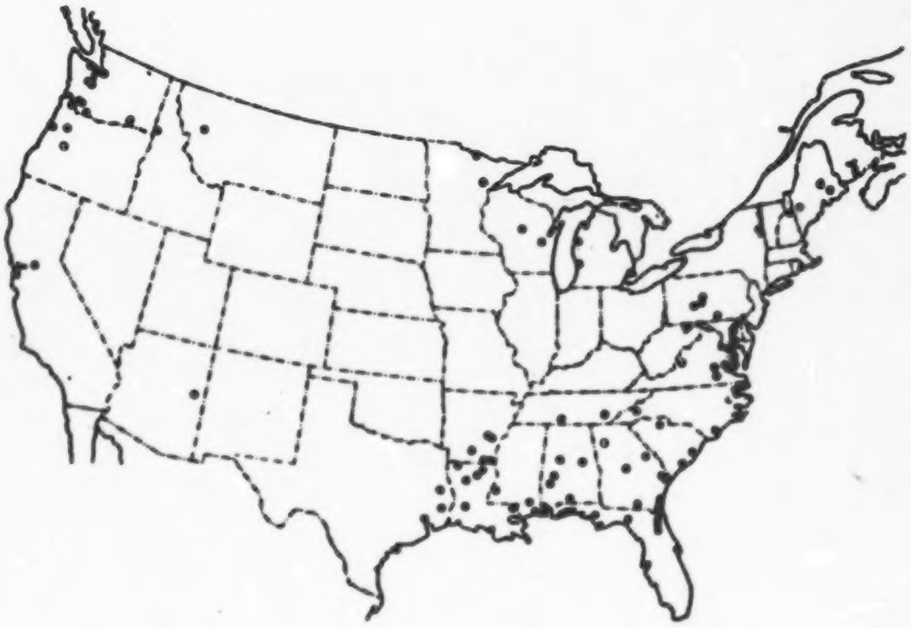

FIGURE 8

Location of Kraft Mills in United States (1957)[68]